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Assessment of the dye-sensitized solar cell

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Abstract

The field of solar electricity, or photovoltaics (PV), is rich in that there are many materials and concepts for converting sunlight into electricity. The technologies accepted as conventional are those well along in the process of commercialization. The dye-sensitized solar cell, developed in the 1990s, is a nonconventional solar electric technology that has attracted much attention, perhaps a result of its record cell efficiency above 10%. This paper reviews the technology, discusses new research results and approaches presented at a recent symposium of many of the world's important dye solar cell researchers, and presents an assessment of the dye-sensitized solar cell in a comparison with current conventional solar electric technologies. It concludes the dye solar cell has potential for becoming a cost-effective means for producing electricity, capable of competing with available solar electric technologies and, eventually, with today's conventional power technologies. But it is a relatively new technology and faces many hurdles on the path to commercialization. Because of its potential, this assessment recommends further funding for research and development (R&D) of the dye-sensitized solar cell technology on the basis of the promising technical characteristics of the technology, a strong US and worldwide research base, positive industry interest, and today's relatively small funding allocation for its R&D.

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1. Introduction

The dye-sensitized solar cell is a nonconventional solar electric technology that gained the attention of the photovoltaic community with the appearance of a 1991 publication in Nature [1]. The dye cell operates quite differently from conventional solar cells, yet researchers have already demonstrated efficiencies greater than 10%. Its foundations are in photochemistry rather than in solid state physics, the discipline underlying today's conventional solar cells. Because of the cell's progress and subsequent interest shown worldwide by solar cell researchers and developers, it is important to conduct an assessment of the dye-sensitized solar cell's competitiveness with conventional solar electric technologies.

Historically, solar cell operation was first discovered in a photochemical cell. The French scientist Becquerel, who discovered the solar electric effect in the 1830s, referred to his device as a 'pile' or 'cell' that produced electric current when exposed to solar radiation [2]. Becquerel's solar cell was an electrolytic cell made up of two electrodes placed in an electrolyte, in which the current increased when the cell was exposed to light. Becquerel distinguished the behavior of this solar cell from that of a

thermocouple (*pile thermoelectrique*) in that the solar radiation and not solar heating produced the cell's direct current. Like batteries, solar cells produce direct electric current (DC) that needs converting to alternating electric current (AC). *Solar cell* is still a good description of the solar electric devices made in the research laboratory, and *solar electricity* is an easily understandable term for the technology of converting sunlight into electricity.

However, photovoltaics, or PV, is the term used for many years by technologists in the field. In either case, PV or solar electricity is one of the renewable energy technologies because the sun is a nondepletable resource. Yet PV is not the best name for the technology, especially when describing it to the general public. There are even some technical inaccuracies with the term. While *photo* refers to light, *volt* ignores the fact that amperes are also part of electricity. Strictly speaking, it is the sunlight that produces the amperes of electric current. Also, power in watts is the product of voltage and amperes, so solar power is technically very accurate. Most of this paper will refer to *solar electricity*, *solar electric technologies*, *solar electric power*, or *solar power* rather than PV.

2. Assessment perspective

The assessment of a solar electric technology can be made from different perspectives. Homeowners or business owners may consider purchasing backup electric systems in case their electric utility cannot provide power when they need it. In comparing different backup technologies, the users' assessment may be based on how much electric power they can get for their money, probably measured in $/watt of electric power. Users might then estimate how much fuel will cost in the future for fossil-fueled systems and how much maintenance costs will be. Unless the assessment is done carefully by acknowledging the volatility of future fossil fuel prices and other value attributes, solar electric technologies still cost too much when compared with fossil-fired electric generation technologies. All solar electric companies are well aware of these assessments made by potential buyers. But there is an undeniable trend in that over the long term, solar electric costs have declined and conventional energy costs have risen. This trend helps drive the remarkably consistent 20% or greater annual market growth for solar electric technologies [3].

Investors considering expanding their portfolio to include solar electric manufacturing companies will perform a different assessment. They may look at how much production capacity they can get for their money. In other words, they might evaluate their investment in terms of investment dollars needed per production capacity. For example, a solar cell manufacturing plant capable of producing 100 MW per year might cost $50 million, $100 million, or $300 million depending on the technology requirements. The measure here is also $/watt, but it is watts of production capacity. Investors also may want to know how much money they will make in a reasonably short time period and how much risk is involved. There are other factors as well, such as the strength of the management and technical teams the company employs and the clarity of their market strategy. Energy investors typically make their decision

in comparison with other potential investments in wind, bioenergy, hydroelectric, or nonrenewable energy companies.

A country or government may conduct yet another type of assessment. This is because it is not concerned with making money and because its citizens typically have long-term interests that they expect their government to accommodate. A government's assessment may involve some of the issues a purchaser and investor consider, as well as others, such as societal benefits, environmental impact, and the country's scientific strength and industrial interest in developing solar electric technologies. Governments need to know if investing the taxpayer's money in the technology's development will provide benefits to the country and its citizens. As a technology assessment, it differs from a policy assessment, in which a government might consider the benefits of a policy or tax reduction to expand the market growth of a technology that provides strategic benefits to a country, such as a reduction in reliance on foreign energy sources.

The technology assessment presented here is made in response to a milestone in the US Department of Energy's (DOE) Five-Year Research Plan to assess the dye-sensitized solar cell [4]. The assessment relies heavily on portions of a technical assessment conducted by Novem, a Dutch research agency, for several solar cell technologies. The dye-sensitized solar cell, or more simply the *dye solar cell,* is a nonconventional solar electric technology not presently part of the world's PV market. About 280 MW of solar electric modules were sold in 2000 throughout the world, more than 90% based on crystalline silicon solar cell technology, which is a conventional solar electric technology. The technology assessment made in this report is meant to help government decision makers determine whether or not more funding should be allocated to developing the dye solar cell. Some elements of the assessment may be useful to potential investors, but it will be of little use for the individual considering the purchase of a solar electric system for his/her own needs.

3. The dye-sensitized solar cell: a nonconventional, organometallic, biomimetic, excitonic, nanocrystalline solar electric technology

Researchers had explored the concept of the dye solar cell long before the 1991 breakthrough publication in Nature [1,5]. The significance of this Swiss research was the discovery of a means for making the concept work, in particular attaching the organic dye to the inorganic titanium dioxide, which permitted the efficient transfer of photoexcited electrons from the dye. The conventional solar cell, first discovered in 1954 [6], is a solid wafer-like semiconductor structure in which sunlight is absorbed, creating positive and negative electric charge carriers. The charge carriers are swept from the structure using an internal electric field. Fig. 1 shows two contacts to the solar cell structure, again reminding us of the similarity with battery cells, that conduct the solar-generated electric current to an external electrical load. The dye solar cell has a different structure and operates quite differently.

The dye solar cell, unlike the conventional solar cell, physically separates the absorption and charge-transport processes. The dye cell mimics photosynthesis in

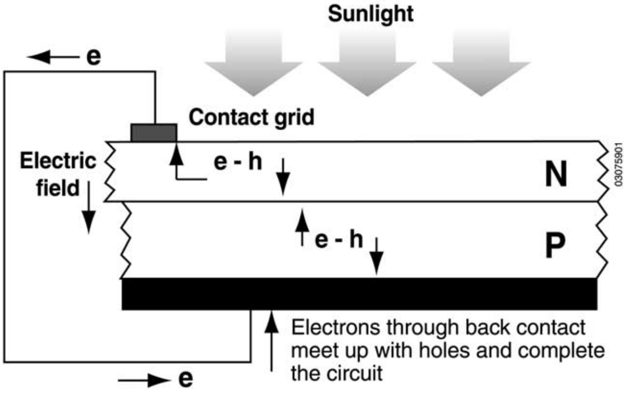

Fig. 1. The conventional solar cell is a solid wafer-like semiconductor structure in which sunlight is absorbed, creating positive and negative electric charge carriers that are swept from the structure by an internal electric field.

that the organometallic dye absorbs sunlight, creating an exciton whose electron is injected extremely rapidly into another medium, a porous matrix of titanium dioxide. In fact, the dye chemistry for this solar cell arose originally from biomimetic considerations based on the model of natural chlorophyll, an organometallic molecule [7]. The other medium consists of a porous structure of titanium dioxide nanocrystals, seen in Fig. 2, that are 10 nm or so in size, and all bonded together, typically through a sintering process. Fig. 3 shows a schematic of the dye solar cell. The dye is attached as a monomolecular layer to the nanoparticle surfaces in the porous matrix. Once the titanium dioxide matrix receives an electron from the dye, the electron diffuses through the matrix to the cell contacts and into an external circuit. Unlike a conven-

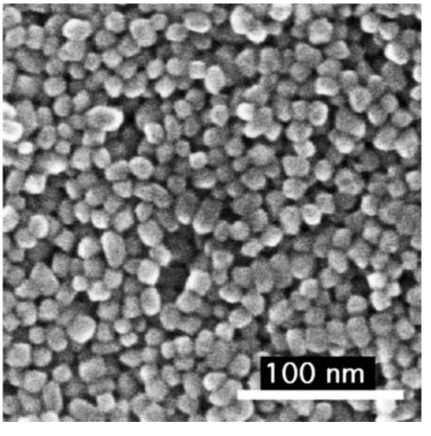

Fig. 2. A porous structure of titanium dioxide nanocrystals that are about 10 nm in diameter, which are bonded together typically through a sintering process.

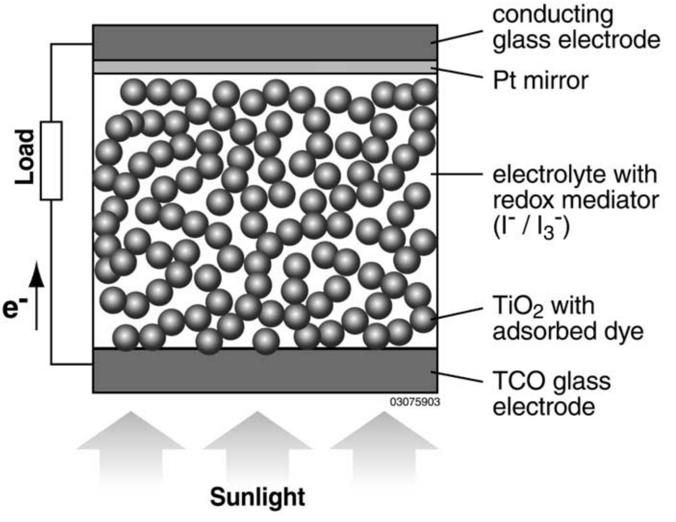

Fig. 3. Schematic of the dye solar cell.

tional solar cell, there is no internal electric field sweeping electric charges to the solar cell contacts. Completing the dye cell circuit requires providing an electron to the dye to replace the one injected into the matrix. The oxidized dye gains an electron by itself oxidizing a mediator — a redox species dissolved in an electrolyte also filling the spaces in the porous matrix. The mediator is, in turn, reduced at the metallic cathode of the solar cell.

In summary, the conventional solar cell is a solid, wafer-like, inorganic semiconductor device in which the minority carriers are critical to the device's operation. Also critical to the operation of a conventional solar cell is an internal electric field created by a homojunction (in the case of crystalline or amorphous silicon) or heterojunction (in the case of copper indium gallium diselenide, cadmium telluride, or GaAs-based materials). The dye solar cell is a nonconventional solar cell with a porous inorganic matrix incorporating an organometallic dye and a liquid electrolyte within the porous spaces of the matrix. It is quite thin, more than 10 times thinner than a crystalline silicon solar cell. It is a biomimetic device in that the dye mimics essential aspects of photosynthesis. It is a nanoparticle device in that the matrix is made from nominal 10-nm diameter particles. It does not incorporate an internal electric field (although future versions might), and it is a majority-carrier device because the electrons are injected into n-type titania. Finally, positive charge transport occurs through ion transport in the electrolyte, rather than hole conduction. Gregg [8] has written a more extensive discussion of the differences between conventional inorganic and nonconventional organic solar cells, including the dye cell. The dye solar cell is a dramatic example of a nonconventional solar cell; yet, its record efficiency has been confirmed at the National Renewable Energy Laboratory (NREL) at 10.4%, considered to be above the significant threshold efficiency for any new solar electric

technology [7]. As we shall see in following paragraphs, several research avenues can increase its efficiency.

One fundamental difference between the operation of conventional and dye solar cells can be illustrated using the following equation from Gregg's discussion of the operational differences between conventional and nonconventional solar cells [8]

$$J_n = n\mu_n\nabla E_{cb} + qD_n\nabla n$$

where the electron current density, J_n, is proportional to the gradient of the conduction band edge, ∇E_{cb}, and the electron concentration gradient, ∇n, in turn proportional to the chemical potential gradient. The remaining terms are the electron mobility, μ_n, the electric charge, q, and the diffusion coefficient, D_n. In conventional solar cells, $\nabla E_{cb}\neq 0$ due to a p–n junction, whereas in the case of no band bending, a solar electric effect can still be achieved if light absorption results in an electron concentration gradient. This is the case for current flow in the titanium dioxide matrix of the nonconventional dye-sensitized solar cell. Another important difference is the means of separating electrons and holes. The only way to separate free electrons and holes in a conventional solar cell is with an electric field. But in an organic solar cell, the more effective means of separation of electrons and holes is the result of the dissociation of excitons — electron–hole bound states created by light absorption. Exciton dissociation can occur at an organic/organic or an organic/inorganic interface, such as the dye/TiO_2 interface in the dye cell. It is the mechanism for charge separation in the dye cell. Dissociation of the exciton, electron injection into the titania, and subsequent electric current in an electric-field-free titanium dioxide matrix is a fundamentally different mechanism than that of a conventional solar cell.

4. Recent dye cell research

An Electrochemical Society (ECS) symposium, Photovoltaics for the 21st Century, II, convened in March 2000 in Washington, DC. The symposium highlighted the research from more than a dozen of the world's eminent researchers and developers of the dye-sensitized solar cell. One aspect of a technology assessment from a government program perspective is identifying research groups that have been contributing to the technology's progress. Another aspect is the potential for improvement through additional research. The ECS symposium, cosponsored by DOE and NREL, provided a snapshot of the important dye solar cell research under way throughout the world. The researchers invited to the dye-cell session of the ECS symposium were selected from more than 70 dye solar cell presenters at the Thirteenth International Conference on Photochemical Conversion and Storage of Solar Energy held in Snowmass, Colorado, in August 2000. The dye-sensitized solar cell presentations comprised a significant portion of more than 300 presentations at the conference. The following discussion of research results at the ECS symposium is presented by group rather than by technology issues.

4.1. Ecole Polytechnique Fédérale de Lausanne (EPFL)

EPFL, located in Lausanne, Switzerland, is the best-known of the research groups at the symposium. It is led by Michael Grätzel and has about 20 researchers. EPFL has a number of funding sources, including the United States Air Force Research Laboratory. As mentioned earlier, Grätzel and O'Regan published the breakthrough dye-sensitized solar cell paper in 1991 [1]. Their early work arose out of an interest in artificial photosynthesis or biomimetics. The prototype of an energy-absorbing dye provided by nature is chlorophyll, a molecule consisting of a central magnesium atom surrounded by a nitrogen-containing porphyrin ring. Emphasizing the significance of the chlorophyll structure in nature is a similar structure in blood — hemoglobin — the oxygen-carrying molecule containing iron. Although nature confines itself to magnesium and iron for its principal pigments, other metallic elements can be incorporated into synthetic porphyrin dyes. Clark and Suttin used a tripyridyl ruthenium complex in 1977 to sensitize titanium dioxide, but the dye was in solution and charge transfer through the solution was very inefficient [7]. In 1980, the idea had emerged of bonding the dye to the metal oxide surface through an acid carboxylate group [7]. This bonding facilitated charge transfer by electron injection. It is now known that an electron passes from the dye molecule through the bridging carboxylate group to the semiconductor substrate within picoseconds, faster than competing recombination processes. Of the hundreds of dye molecules explored over the past decade, one of the most effective is $RuL_2(NCS)_2$ (L=bipyridyl), often called 'N3', as it was the third dye tried by Nazeeruddin at EPFL.

EPFL holds the record for the highest dye cell efficiency (10.4%), confirmed at NREL under air-mass (AM) 1.5 sunlight [7]. It is also responsible for the development of the state-of-the-art black dye in which L_2, the bis-bi-pyridyl ligand system, is reduced to ter-pyridyl and a thiocyanate group is added. The black dye's spectral sensitivity extends throughout the visible and into the infrared ranges, approaching the ideal absorption edge position (1.4 eV) for optimal solar energy conversion. The bonding of the Ti ion to the dye's carboxylate group has also been optimized by adding a suitable salt, permitting higher temperature thermal treatments to 300°C during manufacturing for subsequent bonding, sealing, and curing processes.

EPFL's recent work explores an innovative configuration in which the n-type nanocrystalline titanium dioxide is contacting an organic p-type semiconductor in what they have called a *sensitized nanostructured heterojunction* [7]. This innovative structure might enhance electron transport, and perhaps injection, because of the heterojunction's electric field. And the organic semiconductor replaces the liquid electrolyte's function as a positive charge conductor.

The group has licensed their technology to at least eight companies and thus has acquired an awareness of its commercialization potential. One important commercialization issue is the device's lifetime. The EPFL group has investigated and contributed to the long-term stability of the device. With adequate cell sealing and the addition of suitable solvents in the electrolyte formulation, the system has been able to pass standard stability qualification tests for outdoor applications, including ther-

mal stress for 1000 h at 85°C. The expected lifetime is presently beyond 10 years, again quite respectable for a relatively new solar electric technology.

4.2. University of Bath

The University of Bath research effort is directed by Lawrence Peter. Their presentation included a comprehensive summary of the unusual transport properties that distinguish dye cells from conventional solid-state devices [9]. For example, charge transport in the electrolyte phase takes place by ion transport, a relatively slow process leading to ionic diffusion transit times of the order of 0.1 s. This study, however, focuses on understanding electron charge transport, trapping, and recombination so that more efficient dye cells may be realized. The University of Bath group found that because of remarkably small electron diffusion coefficients, the diffusional transit time for electrons in a typical 10-μm thick titanium dioxide film is of the order of milliseconds at AM 1.5 illumination, but as slow as 100 s at light intensities some seven orders of magnitude less. As noted in their paper, it is surprising that an efficient solar cell can be based on a system that involves such slow charge transport. Also, there is an increase in electron lifetime with decreasing light intensity, which partially explains a reduction in cell efficiency that is much smaller than might be expected at low light intensities. From another point of view, the dye cell performs well in low light levels, which presents opportunities to develop indoor applications.

This study of photovoltage decay followed by short-circuit extraction of remaining electron charge permits the derivation of information about trapped electron charge and its corresponding trap distribution. Electrons are evidently trapped at levels in the bandgap, and the assumption is that these levels are associated with surface states present at the high internal surface area of the nanocrystalline oxide ($\approx$100 m^2/g). These levels are responsible for the retardation of electron transport that is characteristic of dye cells in that diffusion takes place through electron trapping and detrapping processes.

4.3. Emory University

Emory University's group, headed by Professor Tianquan Lian, reported on their experimental studies of interfacial charge separation and charge recombination in two classes of sensitized nanocrystalline films [10]. Their work was funded by DOE's Office of Science and the National Science Foundation (NSF). One class includes the dye-sensitized, wide-bandgap semiconductor, nanocrystalline films used in Grätzel solar cells. The second contains conjugated polymer/nanocrystalline thin-film composites for completely solid-state cells (the MEH-PPV is also the hole transporter). They made measurements on their own samples of MEH-PPV/SnO_2 and compared them with measurements on their dye-sensitized nanocrystalline thin films of TiO_2, SnO_2, and ZnO. Their experimental results show that for both systems, charge separation can be very rapid and efficient (some 300 ps), whereas charge recombination is much slower (microseconds). For example, for MEH-PPV/TiO_2, the electron transfer is believed to be substantially faster than the rate of polymer

exciton decay because transfer has been demonstrated and the polymer photoluminescence is quenched. The Emory technique, using femtosecond mid-infrared (IR) spectroscopy, leads to direct monitoring of injected electrons and substantiates this belief. The comparison is intriguing because they have shown that subpicosecond electron injection from dye to semiconductor is possible with a favorable electronic coupling of the electron-donating and -accepting orbitals and/or a large density of accepting states. But for the MEH-PPV nanocrystalline films, the electron injection is just as fast, yet there are no covalent linkages between MEH-PPV and the SnO_2. The fast charge separation and slow recombination results, like those in dye-sensitized nanoporous films, show that conjugated polymer/inorganic semiconductor nanoporous film composites have promise for solar electricity production.

4.4. ChemMotif, Inc.

ChemMotif, a small business headed by Mark Spitler in Concord, Massachusetts, has been funded by the DOE's Small Business Innovative Research program for research and development of dyes for the dye-sensitized solar cell. The company explored the use of different cyanine dyes and made devices with higher short-circuit photocurrents than those of cells using the well-known N3 dye [11]. The trade-off between broad-band absorption and extinction coefficient for a single dye like N3 leads to slightly thicker titanium dioxide films (10 μm) than could be achieved with aggregates of dyes needing only a 4-μm film thickness. High extinction coefficients for monomer dyes, such as rhodamine, oxazine, thiazine, and cyanine, are associated with very narrow absorption bandwidths. ChemMotif tried to circumvent this obstacle by using aggregates of organic dyes with high absorption over a greater portion of the spectrum. Their work focused on the use of different carboxylated cyanine dyes. They measured absorbance versus wavelength for 14 dyes and their combinations by exploring the structure of the tether of the dye to the titanium dioxide, the terminal heterocycle on the chromophore, the length of the methine bridge, and substituents on the molecule. Some dye pairs did not mix and appeared to collect in different regions on the nanocrystalline surface. They observed the degree of aggregation of the cyanine dyes on the surface to be highly dependent on the procedure for attaching the dyes to the titanium dioxide. An enlightening observation in their work is that some of their heterogeneous collections of dye molecules are used in photography in panchromatic films. This presentation hinted at the large number of dye molecules possibly beneficial to the dye solar cell concept and suggested that dye aggregates may be even more important.

4.5. National Renewable Energy Laboratory (NREL)

The NREL group, under the leadership of both Arthur Nozik and Arthur Frank, is probably the strongest in the US. NREL presented three papers at the ECS symposium, two on electron transport and one on a new family of dyes [12–14]. The NREL team recently measured a preliminary 9.18% efficiency for a dye cell using a titanium dioxide film deposited by screen printing, possibly the highest efficiency

by any group for films prepared by screen printing. This group has been jointly funded by DOE's Office of Science and Office of Energy Efficiency and Renewable Energy.

The NREL group has modeled electron transport using a random walk analysis [12]. In their introduction, they state that the reason transport of photoinjected electrons in the TiO_2 occurs by diffusion is because of the absence of any electric field across the film due to screening by the electrolyte. The collection time for electrons is on the order of milliseconds, much slower than collection times in single-crystal titanium dioxide. The slow collection time is attributed to electrons undergoing many trapping–detrapping events in trap states believed to be on the surface, although the trap states could just as well be inside the nanoparticles. Another attribute of the dye cell system is the coupled motion of electrons and ions moving in opposite directions — ambipolar diffusion. A consequence of ambipolar diffusion is that a current can only be measured in the external circuit upon the arrival of charge carriers at the electrode; this is called an *arrival current*. Their modeling and corresponding experimental results support the concept of an arrival current, as well as multiple trap states with an exponential distribution [13]. This experimental agreement suggests that even shallow traps, owing to their relative abundance, can contribute significantly to the overall transport kinetics.

Another NREL study described a new generation of perylene-based dyes that may make excellent photosensitizers of nanocrystalline titanium dioxide [14]. Although the perylene dye cell efficiencies are low — about 1% — they are reported for the first time in this paper. Perylenes are inexpensive and durable dyes, which is important because the widely used N3 dye is presently quite expensive, more expensive per square meter than glass. Its high price is a consequence of its limited use only in the dye solar cell.

4.6. California Institute of Technology

Caltech's group, led by Nathan Lewis, has been funded by the DOE's Office of Basic Energy Sciences, the NSF, and DuPont. They were recently awarded funding under NREL's Photovoltaics Beyond the Horizon program. Their presentation focused on electron-transfer dynamics using different transition elements, either Os or Ru, in the dye [15]. The dynamics in the dye cell span many orders of magnitude, from tens of femtoseconds to milliseconds, and require a combination of different techniques to study them. The group studied electron injection, charge recombination, and iodide oxidation for different Ru and Os sensitizers. Absorption involves promotion of an electron from the metal-based d orbitals to the bipyridyl-based π^* orbitals. Their work substituted different types of ligands for five sensitizers to explore the electron donation process, charge recombination, and sensitizer regeneration. They looked at oxidized sensitizer regeneration rates for different electrolytes. Charge recombination had higher rate constants for sensitizers having more negative M(III)/M(II) ground-state reduction potentials. Their study concludes that overlap between the solar spectrum and sensitizer absorption spectrum, although clearly important, needs to be considered in light of the importance to optimize sensitizer

regeneration dynamics with respect to charge recombination when charge recombination is limiting cell performance.

4.7. Imperial College

The Imperial College group, under the direction of Professor James Durrant, reported on new measurements of recombination of photoinjected electrons directly with oxidized species in the redox electrolyte [16]. This work supplements their previous studies of recombination of the injected electrons directly with dye cations prior to their re-reduction by I^-. They measured the transient change of light absorption by their samples in response to a laser excitation source (337 nm) and under the varying experimental conditions. Their recent results show an influence of trapping and detrapping of electrons within the titanium dioxide particles on the kinetics of this recombination path between the photoinjected electrons and the electrolyte. Other studies have shown that electron transport in the nanocrystalline titanium dioxide is mediated by trapping in intraband defect states. The Imperial researchers observe two types of recombination behavior, depending on the iodine concentration. In the low I_2 limit, they observe single-exponential kinetics, consistent with a scarcity of holes in the electrolyte. In the high concentration limit, they observe stretched-exponential behavior consistent with trap-limited electron diffusion within the titanium dioxide becoming the rate-limiting step.

4.8. Sustainable Technologies International Pty Ltd (STI)

STI, whose president and CEO is Gavin Tulloch, has worked with the EPFL group for several years and has licensed the EPFL technology. At the ECS symposium, STI announced construction of the world's first dye cell manufacturing facilities, funded mainly by private investors but partly by the Australian government [17]. Testing procedures are critical to the successful technology development of crystalline silicon modules, and STI wants to identify critical failure mechanisms pertinent to the dye cell. The STI presentation focused on the development of accelerated ultraviolet (UV) testing procedures for dye-sensitized solar cells for an initial product with a minimum warranty of 7 years. Their first product is expected to be an exterior building panel marketed as a solar wall panel. They identified UV radiation and elevated temperatures as the dominant stress factors for dye-sensitized cells and modules. They began tests with areas of 1 cm^2 and described plans for future testing of 100 m^2 panels. They found good solar cell durability with appropriate concentrations of iodine and lithium iodide in the electrolyte. Their 600-h temperature studies showed a surprising increase in dye cell performance with temperature. Specifically, they measured a 25% power increase between 30 and 65°C, with 80°C power still 15% higher than the baseline temperature power.

4.9. Johns Hopkins University

This group was funded by NREL for dye solar cell research soon after the 1991 discovery of the concept. Their recent work was funded by DOE's Office of Science

and the NSF. They were recently awarded funding under NREL's Photovoltaics Beyond the Horizon program for a new solar cell concept based on molecular chromophores, antenna-like sensitizer molecules. Their ECS presentation described new approaches to increase the efficiency of the dye solar cell to 15%.

The Johns Hopkins group points out that if the spectral response of the dye solar cell can be increased to 1100nm, an efficiency of 20% has been predicted [18]. They discussed two approaches for optimizing the photocurrent by tuning the chromophoric ligands and/or the nonchromophoric ligands in the Ru(II) dye molecule (sensitizer) used in the most successful dye solar cells. The current state-of-the-art dye solar cell is composed of the coordination compound *cis*-$Ru(dcbH_2)_2(NCS)_2$, where $dcbH_2$ is 4,4′-$(CO_2H)_2$-2,2′-bypyridine. This is the compound called N3. They point out that the metal-to-ligand charge-transfer (MLCT) absorption can be extended to longer wavelengths by appropriate substituent changes on chromophoric ligands. But moving the carboxylic acid groups from the 4 and 4′ positions led to some spectral enhancement, but also to a lower efficiency than N3. The group referenced the EPFL work whereby a novel Ru(II) complex increased the spectral sensitivity to about 920 nm, but the benefits of increased spectral sensitivity were offset somewhat by the lower extinction coefficient of the dye. Nevertheless, this dye resulted in the record 10.4% efficiency solar cell. Nonchromophoric ligands are not directly involved in the MLCT absorption but can be used to change the color of the compounds. Drawbacks in different ligands can include poor electron injection yields and sluggish iodide oxidation rates.

The group observes that the open-circuit voltage is determined by the energetic difference between the Fermi levels of the illuminated transparent conducting oxide contact to the nanocrystalline titanium dioxide film and the platinum counter electrode where the iodide is regenerated. The platinum electrode's Fermi level is expected to be close to the energy of the redox couple in the solution. An interesting possibility is to select a redox couple with a more positive equilibrium potential. This will decrease the energy loss associated with dye regeneration and may increase the open-circuit voltage. They propose a thiocyanate/thiocyanogen couple to replace the iodide/triiodide electrolyte, which could lead to 16% efficiency if the fill factor and current remain unchanged. They discuss other possible ways to increase the photovoltage, including Fermi-level tuning by adsorption of cations, inhibiting charge recombination of injected electrons with iodide oxidation products at the TiO_2 electrode, reduced sensitizers that are stronger reductants than their excited states, and the possible use of sensitizer-antenna molecular devices. Their experiments with a branched antennae sensitizer on TiO_2 in aqueous solution at pH 3.5 resulted in significant photocurrents. Subsequent experiments on this complex anchored to nanocrystalline TiO_2 gave a global conversion efficiency of about 7%. They conclude that, unlike the photocurrent, the open-circuit photovoltage and thermodynamics are not optimized because only about one third of the free energy stored in the molecular excited state of the sensitzer is captured in the operational cell. They believe there are several approaches to extend the efficiency of the dye-sensitized cells to beyond 15%.

4.10. Ångström Solar Center

The Ångström Solar Center (ÅSC) in Uppsala, Sweden, described a new method for manufacturing the dye-sensitized solar cell using only room-temperature processing [19]. The ÅSC group began work on the dye cell in 1996 with the goal of developing the technology so that it would be better than competing thin-film technologies, like amorphous silicon or copper indium diselenide. They chose a very ambitious goal of manufacturing the dye cell on a flexible plastic substrate at room temperature. They started with glass substrates, but reported in their ECS paper on a process using plastic substrates that reproducibly led to 4.1%-efficient solar cells (at 0.1 sun). A key process step is the fabrication of the titanium dioxide porous matrix. Instead of sintering, the titanium dioxide nanoparticles are compressed on the plastic substrate using static pressure. They conclude that it is quite plausible for a roll press to be integrated into a continuous room-temperature production line for dye-sensitized solar cells. Since the vacuum processes of today's thin-film solar cell technologies require major investments for their production facilities, the development of nonvacuum processes for the dye solar cell can lead to substantially lower manufacturing investment costs and subsequently lower technology costs.

5. Beyond the Horizon Awards

Awards selected from proposals submitted in response to the 2000 competitive procurement entitled *Photovoltaic Technologies Beyond the Horizon* nurture basic scientific research to identify and develop nonconventional breakthrough solar electric technologies able to compete with other large-scale energy technologies currently in use. Investment in basic scientific research is a long-term economic imperative for technological strength, as science and technology have been — and will continue to be — the engine of economic growth. The premise of this research program is that PV innovation has not gone as far as it can and that new, viable PV technologies exist 'beyond the horizon' of our present knowledge. Fundamental and exploratory research is needed to see what can be next. The basic scientific research in the project is directed toward the goal of generating inexpensive electricity from sunlight. It is expected to generate new knowledge with practical application. Of 16 awards announced in April 2001, three projects related to the dye-sensitized solar cell concept received funding [20–22]. The three projects, described later, started in July 2001 and are planned to last for three years.

5.1. California Institute of Technology

The research project proposed by Caltech is titled 'Efficiency Improvements of Dye-Sensitized Nanocrystalline TiO_2 Solar Cells' [20]. The researchers will try to better understand how to alter or replace the existing molecular components of the cell with alternatives that will simultaneously provide higher photovoltages, while retaining the high photocurrents exhibited by the present system. The goal is to

develop alternative material combinations to the well-studied nanocrystalline titanium dioxide systems based on a Ru(II) dye, a nonaqueous electrolyte, and the I_3^-/I^- redox couple. This combination of materials results in a thermodynamic limitation on the photovoltage, due to a less-than-optimal separation between the Fermi level of the redox electrolyte and the conduction band of the titanium dioxide.

The Caltech group will explore two strategies to improve efficiency of the cell. In one approach, they will try nanocrystalline semiconductors with a more negative conduction band energy along with appropriately modified sensitizers. The second strategy will use redox mediators with more positive Fermi levels. In implementing this work, they will focus on three areas: (1) understanding the role of the energetics of the semiconductor and dye around the I_3^-/I^- redox couple, (2) determining the mechanism of the I_3^-/I^- couple, and (3) determining the role of injection and recombination on performance. The goal of Professor Nathan Lewis, the principal investigator, is to more than double the efficiency of the dye-sensitized solar cell, while maintaining the stability achieved in its current configuration.

5.2. Johns Hopkins University

The proposal from Johns Hopkins, jointly with North Carolina State University, is entitled ‘Solar Energy Conversion with Ordered, Molecular, Light-Harvesting Arrays’. The proposal describes a new molecular approach in which prefabricated chromophore arrays will be organized on electrode surfaces for use in regenerative solar cells [21]. The approach is new, but borrows from lessons learned in dye-sensitized and organic solar cells. The technique takes advantage of recent advances in synthetic chemistry that allow the rational construction of linear chromophore arrays. Professor Gerald Meyer is the principal investigator and will be working with NCSU’s Professor Jonathan Lindsey. NREL funded Meyer and Peter Searson in the 1990s to study the dye-sensitized solar cell. The project’s specific objectives are to (1) use porphyrins, phthalocyanines, chlorins, and derivatives of these compounds in linear, rigid, chromophore arrays; (2) identify linkers and surface binding groups for the chromophores; (3) develop an understanding of the steps in the proposed energy conversion process, primarily through electrochemical and spectroscopic studies; and (4) synthesize linear chromophore light-harvesting arrays in solar cell form. The solar cells will be thin (less than a micron thick), flexible, and will not use an electrolyte. They hope their approach will lead to greater than 10% efficiency within their project’s time frame of three years.

5.3. DuPont

The DuPont proposal focuses on the ‘Development of a Solid-State Electrolyte for Dye-Sensitized Solar Cells’ [22]. Led by Thomas Griffin, the research group recognizes that the replacement of the liquid electrolyte in today’s highest-performing dye-sensitized solar cells offers several advantages for the technology. But there are major research challenges associated with synthesis, stability, electron-transfer thermodynamics, transport rates and reaction kinetics, compatibility with

other anode components, and avoidance of shorting and recombination. Candidate materials include, but are not limited to, gel ionomer systems, polyalkylcarbazoles, polythiophenes, polyanilines, polyalkythiophenes, and amine hole-transport materials. Part of DuPont's exploration includes electrolyte synthesis through the DuPont 'Building of Materials Library'. Another aspect of this project involves DuPont's collaboration through a subtier contract with Michael Grätzel at EPFL and Gavin Tulloch at STI to conduct an analysis of materials' costs, develop a strategy for cost reduction, and estimate the investment cost for a 100-MW manufacturing plant.

6. An assessment framework for the dye cell

In May 2000, the Netherlands Agency for Energy and the Environment (Novem) completed a technology evaluation of thin-film solar cells referenced to multicrystalline silicon, the principal conventional solar cell technology in today's marketplace [23]. This was a carefully thought-out attempt to compare the strengths and weaknesses of several different solar electric technologies to guide solar electric research efforts in the Netherlands. Researchers and companies quite naturally tend to highlight the strengths of the technology they are developing without carefully considering drawbacks. Novem developed an impartial assessment framework with criteria and criteria weighting, reviewed the literature to determine appropriate values for the criteria, and involved more than 20 PV experts in the evaluation and its review.

The Novem assessment provides an excellent framework for considering all of the issues relevant to assessing the potential of the dye solar cell. Further, the results of the assessment provide a comparison of how the dye solar cell fares in relation to conventional solar electric technologies. For these reasons, it is instructive to review the details of the Novem assessment.

The Novem evaluation was conducted with respect to cost, applicability, sustainability, and compatibility within the Dutch PV infrastructure. Within the cost category, the following three criteria were evaluated: module production cost, efficiency, and risk, with respective weights of 0.5, 0.2, and 0.3. Applicability also had three criteria: design and color, product diversity, and market share, with respective weights of 0.4, 0.3, and 0.3. The sustainability category evaluated energy payback time, availability of resources, and toxicity, with respective weights of 0.4, 0.4, and 0.2. Their final criterion, PV R&D in the Netherlands, evaluated the number of people active in industry and the number active in universities and research institutes. All criteria values in the tables below are taken directly from the Novem assessment. No attempt was made to evaluate the number of researchers working on the dye solar cell in the US; the number is undoubtedly small. There has, however, been some industry interest in the US. At least three small US companies have had SBIR funding for dye solar cell development and one large one (i.e. DuPont) has used its own funds for some initial exploratory research. However, ignoring this criterion in the Novem assessment leaves an enlightening technology comparison between the dye solar cell and the conventional solar cell technologies heavily funded by DOE.

The Novem assessment of solar cell technologies includes multicrystalline silicon,

amorphous silicon [including a-(Si,Ge):H], thin-film (<50 μm) silicon film made at high temperature, thin-film (<5 μm) microcrystalline silicon made at low temperature, $Cu(In,Ga)(Se,S)_2$, CdTe, and the dye-sensitized solar cell. The reference year for the technology evaluation is 2005, and the benchmark technology is multicrystalline silicon wafers produced by direct casting (specifically ribbons), as well as conventional directional solidification and sawing of crystalline silicon. The present total market share of crystalline silicon is 85%.

Novem conducted the evaluation by asking 21 Dutch and foreign PV experts to score the technologies using the various criteria. Although most (14) of the experts came from the Netherlands, interviews and scores were also obtained from seven foreign experts in the US (including NREL), Germany, England, and Japan.

Table 1 summarizes the input parameters for the Novem evaluation of cost and sustainability, the key technical criteria values. Cost/Watt is determined in European currency units per peak Watt, but can be considered to be in US $ per peak Watt with only a 10–15% discrepancy. The cost estimates, efficiencies, and energy payback times are based on Novem's literature reviews. Novem conducted an extensive analysis of risk. It was determined by a maturity score based on the status of the technology's process steps in terms of industrial, pilot, prepilot, and laboratory. Resource limits, in peak gigawatts, are based on the assumption that the total reserves of the limiting element will be used to manufacture the solar electric modules. Again, a literature review served as the basis for identifying the limiting element, the amount needed per unit area, and the total reserves. Although toxicity can depend on exposure routes, the Novem analysis is based on the assumption that materials in the panel are emitted to air as a result of fire. The score is determined from a formula including the mass of metals and organic materials, the toxicity factors for both, and

Table 1
Criteria values for cost and sustainability

Technology	mc-Si	LT-film Si	HT-film Si	a-(Si,Ge):H	CIGS	CdTe	Dye cell
Criteria values							
Cost							
Cost/Watt ($/Watt)	0.88–1.22	0.55–0.75	0.98	0.55–0.75	0.70–0.94	0.86–1.24	0.60
Efficiency (%)	16	11	14	10	12	10	8
Risk (expert's determination)	1.0	1.6–2.6	3.0–4.4	1.3–1.9	1.4–2.2	1.6–2.6	2.6–4.6
Sustainability							
Energy payback (year)	2.3–4.1	1.9–3.0	4.7	1.9–3.0	1.3–1.8	0.5–0.9	1
Resource limits (GW)	22,400	165,000	19,600	380	56–240	310–430	4800–5700
Toxicity (kg/m^2)	0.086	0.0045	0.086	0.0048	0.47	2.5	0.021

estimates for the emission of the materials in a fire. The units for toxicity correspond to the human body mass that is contaminated to the maximum tolerable limits as a result of burning 1 m^2 of module.

Normalizing these scores to those of multicrystalline silicon leads to Table 2, which includes the Novem weighting factors. For criteria with a large negative indication (cost/Watt, risk, energy payback, and toxicity), the reciprocal value of the average is used. Due to the wide variation in energy payback times, available resources, and toxicity, some technologies scored extremely high in the sustainability category. So that these results will not overshadow the overall evaluation, the maximum score for each sustainability subcriterion was limited to 2.

The applicability category criteria try to evaluate marketability issues and included design and color, product diversity, and market share. Interviews with experts from industry and R&D institutions determined the status expected in 2005. Design and color has added value in some markets, whereas product diversity measures the flexibility of a possible production facility to serve different markets with a single production line. Market share, partially correlated with product diversity, assesses the potential market for each technology.

Using the above weight factors leads to the final technology assessment matrix in

Table 2
Normalized criteria values for cost, sustainability, and applicability

Technology		mc-Si	LT-film Si	HT-film Si	a-(Si,Ge):H	CIGS	CdTe	Dye cell
Normalized criteria								
Cost	Weight							
Cost/Watt	0.5	1.000	1.615	1.290	1.615	1.280	1.000	1.750
Efficiency	0.2	1.000	0.688	0.875	0.625	0.750	0.625	0.500
Risk	0.3	1.000	0.476	0.270	0.625	0.556	0.476	0.278
Sustainability								
Energy payback	0.4	1.000	1.306	0.681	1.306	2	2	2
Resource limits	0.4	1.000	2	0.875	0.017	0.007	0.017	0.234
Toxicity	0.2	1.000	2	1.000	2	0.183	0.034	2
Applicability								
Design, color	0.4	1.000	1.071	1.000	1.354	1.354	1.382	1.180
Product diversity	0.3	1.000	1.018	1.000	1.233	1.233	1.320	0.920
Market share	0.3	1.000	0.881	1.000	1.011	0.810	0.649	0.675

Table 3. Table 3 also shows US DOE funding for these technologies during the fiscal year 2000. The contrast between the technology total scores and funding clearly shows the influence of nontechnology factors in making program decisions. We will discuss these factors later.

7. Discussion of the dye cell assessment

The technology total scores from the Novem assessment show the dye-sensitized solar cell competes quite well with the principal solar electric technologies in today's marketplace or those under serious development. Although each technology has weaknesses, there are some interesting insights behind the high final score for the dye-sensitized solar cell. The dye cell is one of the newest of the technologies considered in the Novem assessment, and the high risk score for the dye cell in Table 1 is mainly due to the relatively recent discovery of the technology and its subsequent comparative immaturity. If the history of other solar electric technologies is an accurate gauge, the low efficiency score of the dye cell is also a result of the newness of the technology. In other words, additional research (and research support) will likely lead to higher efficiencies and lower risk. Note that six years passed between the year of the initial publication in 1991 until the first report of an efficiency above 10%. For comparison, it took almost 20 years (1963–1982) for this to happen for CdTe-based solar cells, and about seven years for both CIS materials (1976–1983) and amorphous silicon (1976–1983) [24].

The high energy payback score for the dye cell results from a manufacturing process conducted mainly under atmospheric pressure or at low temperature. Although the Novem assessment did not consider the cost of the manufacturing plant, it is understood that the vacuum equipment needed for other thin-film solar cell production and the high-temperature processing equipment needed for multicrystalline silicon solar cells lead to severe limitations in ramping up production capacity. It typically requires \$1/Watt–\$3/Watt to build a manufacturing plant [25,26]. This translates to several hundred million dollars per megawatt of production capacity. Manufacturing plant costs become more critical as module costs approach \$1/Watt.

Table 3
Assessment scores and DOE funding

Technology	mc-Si	LT-film Si	HT-film Si	a-(Si,Ge):H	CIGS	CdTe	Dye cell
Weighted criteria totals							
Cost	1.00	1.09	0.90	1.12	0.96	0.77	1.06
Sustainability	1.00	1.72	0.82	0.93	0.84	0.81	1.29
Applicability	1.00	1.00	1.00	1.22	1.17	1.14	0.95
Technology total score	3.00	3.79	2.72	3.27	2.97	2.75	3.30
US DOE funding (\$000)	12,443	147	1527	8667	6938	6555	215

The cost per megawatt of dye cell production capacity is expected to be much less. DuPont, EPFL, and STI plan to explore how much less dye solar cell plants will cost [22]. Manufacturing plant cost is also a significant financial consideration when very large production capacities are envisaged, especially in relatively short time periods, since large amounts of capital have to be found.

A frequently cited limitation of the dye cell is the liquid electrolyte, which is used for the highest-efficiency dye cells. Although R&D has pretty much resolved this issue through innovative sealing and stabilization procedures, the discovery of a gel electrolyte or a solid-state electrolyte could significantly alter this concern.

The good resource limit score for the dye cell is related to ruthenium, a relatively scarce material. Although rare, so little ruthenium is required (one atom per dye molecule) that about 100 times less mass per square meter is needed than for other thin-film technologies. This outcome leads to the relatively high resource limits scores. The dye cell's toxicity score results primarily from residual toxicities of the back and front cell contact materials.

Finally, all assessments raise questions about the proper evaluation of differing technologies. The Novem assessment is certainly not perfect (for example, capping the sustainability scores is somewhat arbitrary), but it does provide a reasonable framework for quantitatively determining the potential of differing solar electric technologies. Furthermore, a significant number of solar electric researchers and developers were involved in the scoring, weighting, and reviewing the assessment results. Although it might be worthwhile to develop a DOE assessment process and conduct the assessment with more input from US researchers and developers, the Novem assessment procedure provides valuable insight for assessing the technology potential of the dye-sensitized solar cell with respect to other solar cell technologies.

8. Government funding supporting dye cell research and development

We estimated the funding allocated by the US DOE to these technologies for Fiscal Year 2000, which ended on September 30, 2000 [27]. As shown in Table 3, the majority of funds support research and development for single-crystal and multicrystalline silicon solar cell technologies. Another technology based on GaAs compounds and alloys feeds into the highest-efficiency solar cells destined for concentrator modules; these GaAs-based technologies are funded by another \$2.75 million. In the case of the well-funded solar electric power technologies (mc-Si, HT-film Si, a(Si,Ge):H, CIGS, and CdTe), some experts believe private industry provides at least an equal amount of funding for research and development — funds totally separate from their investments in manufacturing plants and commercialization. This 'leveraging' of funds enhances the impact of government funding for technology development and leveraging is less likely for companies just beginning in the technology development cycle. The conclusion, not an unusual one for embryonic technologies, is that the dye-sensitized solar cell is receiving far less funding than mature, conventional technologies. Simply on the basis of its technology strengths, the dye-sensitized solar cell appears as a likely candidate for some additional funding, at

least within the portfolio of solar electric power technologies supported by the US DOE program.

But implementing a decision to increase dye solar cell funding will depend on other factors, not the least of which is the total available annual budget for solar electric R&D. And there are other program issues. Support for the conventional solar electric technologies is important because their impact is near term (1–5 years) as well as mid-term (5–10 years). And there are important stakeholders in the US solar electric companies developing conventional technologies and leveraging the government's funding. Further, the amount of additional funding allocated for dye solar cell work will be dependent on the universities and companies with capabilities to contribute to its development. One way to answer many of these questions is to request research proposals. A competitive Request For Proposals is an excellent means to identify the dye solar cell's key technical research issues, the capabilities of research groups proposing to overcome them, and the amount of funding that could support these efforts. The conclusion remains that in case of an increased program budget, modest additional support for R&D on the dye solar cell will be an excellent option for DOE to consider.

9. Conclusions

The Novem assessment provides a reasonable basis for considering the positive and negative attributes of the dye-sensitized solar cell. Within the assumptions of the Novem assessment, the dye-sensitized solar cell competes well with near-term technologies like CIGS and CdTe, which will be making significant market inroads during the next five years. The dye solar cell also competes well with today's technologies based on multicrystalline and amorphous silicon. Further, the dye solar cell is a higher-risk technology because it is relatively new. Many governments, including the US, consider it to be good policy to support high-risk technologies having the potential to compete with more mature technologies [3]. Our discussion of recent research described a number of promising and potentially significant technology paths for the dye solar cell. Another policy consideration is the demonstrated interest of private industry, both in the US and abroad. With these policy considerations met, the results of the technology part of the Novem assessment, the excellent research taking place worldwide, and the relatively small US funding allocated for this technology, this assessment concludes with the recommendation to increase government support for further research and development of the dye-sensitized solar cell technology.

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